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WITNESS my hand this
Seventh day of November 2003

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Patents Act 1990

PROVISIONAL SPECIFICATION

for the invention entitled:

"Modified Polymeric Compositions"

The invention is described in the following statement:

MODIFIED POLYMERIC COMPOSITIONS

The present invention relates to polymeric compositions which have useful fire resistant properties and which may be used in a variety of applications. The invention also relates
5 to the preparation of such compositions and to their use.

Passive fire protection of structures and components is an area that is receiving increased attention. In this context the term "passive" means the use of materials that impart fire resistance. Passive fire protection systems are used extensively throughout the building
10 and transportation industries and typically function by counteracting the movement of heat and/or smoke, by sealing holes, by prolonging stability of structures to which the system is applied and/or by creating thermal and/or physical barriers to the passage of fire, heat and smoke.

15 One particular area of interest is electric cables for non-aerial applications. These typically consist of a central conductor surrounded by at least an insulating layer. Such cables find widespread use in buildings and indeed form the basis for almost all electric circuits in domestic, office and industrial buildings. In some applications, e.g. in emergency power supply circuits, there is a requirement for cables that continue to operate and provide
20 circuit integrity even when subjected to fire, and there is a wide range of standards for cables of this type. To meet some of these standards, cables are typically required to at least maintain electrical circuit integrity when heated to a specified temperature (e.g. 650, 750, 950, 1050°C) in a prescribed manner and for a specified time (e.g. 15 min., 30 min., 60 min., 2 hours). In some cases the cables are subjected to regular mechanical shocks
25 during the heating stage. For example, they may be subjected to a water jet or spray either in the later stages of the heating cycle or after the heating stage. In real fires parts of a cable will probably be exposed to a wider range of temperatures for even greater variations in duration. To meet a given standard a cable is typically required to maintain circuit integrity throughout the test. Thus it is important that the insulation maintains low
30 conductivity (even after prolonged heating at high temperatures), maintains its shape so it does not shrink and crack, and is mechanically strong, particularly if it is required to

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remain in place during shock such as that resulting from mechanical impact due to water jet or spray exposure.

One method of improving the high temperature performance of an insulated cable has been to wrap the conductor of the cable with tape made with glass fibres and coated with mica. Such tapes are wrapped around the conductor during production and then at least one insulative layer is applied. Upon being exposed to increasing temperatures, the outer layer(s) are degraded and fall away, but the glass fibres hold the mica in place. These tapes have been found to be effective for maintaining circuit integrity in fires, but are quite expensive. Further, the process of wrapping the tape around the conductor is relatively slow compared with other cable production steps, and thus wrapping the tape slows overall production of the cable, again adding to the cost. A fire resistant coating that could be applied during the production of the cable by extrusion, thereby avoiding the use of tapes, would be desirable.

A variety of materials have been used to impart fire resistance to structures and components. The use of compositions based on silicone elastomers has found widespread use. However, these compositions tend to have the associated disadvantage that they are converted to powdery substances when exposed to fire because the organic components of the silicone elastomers are pyrolysed or combusted. The pyrolysis or combustion products are volatilised and leave an inorganic residue or ash that has little inherent strength. This residue is generally not coherent or self-supporting and indeed is often easily broken, dislodged or collapsed. This behaviour mitigates against using silicone elastomers as passive fire protection elements. This means that silicone polymers used as insulation on electric cables must be protected and held in place with physical supports such as inorganic tapes and braids or metal jackets. Compositions in accordance with the present invention may form a physically strong coherent layer around an electrical conductor and therefore do away with the need to use such physical supports.

Specifically, the present invention provides a fire resistant composition which comprises a silicone polymer and inorganic material, and which may be converted into a solid ceramic

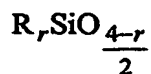
material after firing at elevated temperatures. In this context a ceramic is an inorganic non-metallic solid material prepared by high temperature processing (e.g. above about 400°C). The invention seeks to provide fire resistant compositions which do not undergo any substantial change in dimensions when exposed to fire and which are capable of providing a residual coating that has improved coherence and physical properties across the range of temperatures that would typically be encountered in a fire. Such compositions would have widespread application in providing fire resistance to structures and components thereof. The compositions are particularly useful for providing fire resistant insulation for electrical cables as they may provide suitably high electrical resistivity and breakdown strength, even after prolonged heating at high temperature.

In one embodiment, the present invention provides a fire resistant composition comprising: a silicone polymer; and mica in an amount of up to 30% by weight based on the total weight of the composition, wherein the type and particle size of the mica are selected in order to provide properties appropriate for the intended use of the composition.

It has been found that compositions in accordance with the present invention may form a coherent ceramic product when exposed to elevated temperatures and that this product exhibits desirable physical and mechanical properties. It is a further advantage of the compositions of the present invention that this type of coherent product with desirable physical and mechanical properties can be formed at temperatures well below 1000°C.

The compositions of the invention may be used in a variety of applications where it is desired to impart fire resistance to a structure or component. The compositions are therefore useful as passive fire protection systems. In accordance with the present invention the properties which the compositions are desired to exhibit when exposed to the range of elevated temperatures commonly associated with a fire may be manipulated by suitable choice of the type and particle size of the mica which is used. In other words, the present invention allows the properties of the compositions to be tailored to the intended end use. This is discussed in greater detail below.

The compositions of the present invention include as an essential component a silicone polymer. The nature of the silicone polymer is not especially critical and one skilled in the art will be aware as to the type of polymers which may be used. Useful silicone polymers are described in detail in the prior art including US 4,184,995, US 4,269, 753, US 4,269,757 and US 6,387,518. By way of more specific illustration, the silicone polymer may be an organopolysiloxane composed of units of formula:



in which

- 10 R may be identical or different and are unsubstituted or substituted hydrocarbon radicals, r is 0, 1, 2 or 3 and has an average numerical value of from 1.9 to 2.1.

Examples of hydrocarbon radicals R are alkyl radicals, such as the methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, neopentyl, tert-pentyl and hexyl radicals, such as n-hexyl, heptyl radicals, such as the n-heptyl, octyl radicals, such as the n-octyl, and isooctyl radicals, such as the 2,2,4-trimethylpentyl, nonyl radicals, such as the n-nonyl, decyl radicals, such as the n-decyl, dodecyl radicals, such as the n-dodecyl, octadecyl radicals, such as the n-octadecyl; cycloalkyl radicals, such as cyclopentyl, cyclohexyl and cycloheptyl and methyl cyclohexyl radicals; aryl radicals, such as the phenyl, biphenyl, naphthyl and anthryl and phenanthryl; alkaryl radicals, such as o-, m- or p-tolyl radicals, xylyl and ethylphenyl radicals; and aralkyl radicals, such as benzyl and α - and β -phenylethyl.

25 Examples of substituted hydrocarbon radicals R are halogenated alkyl radicals, such as 3-chloropropyl, the 3,3,3-trifluoropropyl and the perfluorohexylethyl and halogenated aryl, such as the p-chlorophenyl and the p-chlorobenzyl.

The radicals R are preferably hydrogen atoms or hydrocarbon radicals having from 1 to 8 carbon atoms, preferably methyl. Other examples of radicals R are vinyl, allyl, methallyl, 1-propenyl, 1-butenyl and 1-pentenyl, and 5-hexenyl, butadienyl, hexadienyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, ethynyl, propargyl and 1-propynyl. The

radicals R are preferably alkenyl radicals having from 2 to 8 carbon atoms, particularly vinyl.

The end groups of the polymers may be trialkylsiloxo groups, for example trimethylsiloxo or dimethylvinylsiloxo groups, or derived groups where one or more of the alkyl groups has been replaced by hydroxy or alkoxy groups.

The composition may include one or more than one crosslinkable silicone polymer. The crosslinkable polymer can be any one which can be crosslinked by any one of the methods used for commercially available organopolysiloxane polymers including by free radical crosslinking with a peroxide through the formation of ethylenic bridges between chains, by addition reactions including reaction of silylhydride groups with allyl or vinyl groups attached to silicon, through condensation reactions including the reactions of silanols to yield Si-O-Si crosslinks, or using other reactive groups. Depending on the type of silicone polymer used the composition will therefore further comprise a suitable crosslinking agent. Suitable crosslinking agents are commercially available, for example there is a wide range of useful peroxides suitable for use in this application, such as dibenzoyl peroxide, bis (2,4-dichlorobenzoyl) peroxide, dicumyl peroxide or 2,5-bis(tert-butylperoxy)-2,5-dimethylhexene or also mixtures of these, and when appropriate they may be included in the composition during the compounding process.

The silicone polymers that can be used also include platinum catalysed liquid silicone polymers with unsaturated (typically vinyl) side chains that crosslink through the application of heat in an addition reaction. Such polymers are usually supplied as two components that are mixed together just prior to use. The viscosity of these polymers ranges from pourable liquids through to stiff pastes. The silicone rubber compositions may also comprise a room temperature moisture-curable organopolysiloxane (RTV), for which an example is given in more detail in US 5023295. In this case it comprises: (a) an diorganopolysiloxane having terminal hydroxyl groups (b) cross-linking agent having an average of at least 3 hydrolysable functional groups linked to a silicone atom per molecule (c) a condensation catalyst and (d) a platinum metal or compound. Other room temperature

curing systems possessing alkyl silicate and metal salts of carboxylic acids as one part which is combined with the silanol end stopped diorganopolysiloxane and inert filler as the other part, as for example described in US 4184995 will also be included.

- 5 Another type, especially suitable for cable insulation, is where the silicone polymers is of high molecular weight and has vinyl side chains that require heat to crosslink, either through platinum catalysed addition reactions or peroxide initiated free radical reactions. These silicone polymers are widely available commercially from major silicone producers.
- 10 The organopolysiloxane raw materials preferably also comprise reinforcing fillers such as precipitated or pyrogenic silicas and/or non-reinforcing fillers. Further, the surface of these silica type fillers may be modified by straight or branched organopolysiloxanes, organo-chlorosilanes and/or hexamethyl disilazanes.
- 15 Without wishing to be bound by theory, it is believed that compositions in accordance with the present invention form a coherent ceramic product after exposure to elevated temperatures as a result of materials of lower melting point, which may be eutectic mixtures, forming at the interface of the mica particles and inorganic compounds formed from the silicone polymer. Ordinarily, silicon dioxide particles and other compounds
- 20 formed from decomposition of silicone polymers and the mica each have melting points well above 1050°C. However, the eutectic that forms at the interface melts at a lower temperature. This material is believed to act as a "bridge" between the silicon dioxide particles and/or other compounds formed from decomposition of silicone polymer and the mica, thereby solidifying the composition at the firing temperature. Upon cooling, a
- 25 coherent ceramic product is formed and this has been found to be self-supporting and able to withstand at least minor mechanical impacts or shocks.

The compositions in accordance with the present invention include mica as an essential component. The two most common classes of commercially available mica are muscovite

30 and phlogopite. Muscovite mica is a dioctahedral alkali aluminium silicate. Muscovite has a layered structure of aluminium silicate sheets weakly bonded together by layers of

potassium ions. It has the following composition $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$. Phlogopite mica is a trioctahedral alkali aluminium silicate. Phlogopite has a layered structure of magnesium aluminium silicate sheets weakly bonded together by layers of potassium ions. It has the following composition $\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$. Both mica types are typically present in the form of thin plates or flakes having sharply defined edges.

Compositions containing phlogopite mica display greater mechanical strength when heated to about 1000°C to form ceramics. However, they also show greater shrinkage than those containing muscovite mica. The use of muscovite mica is preferred in applications where greater dimensional stability is required. It has been found that the high temperature electrical properties of silicone polymer compositions of the present invention are slightly better if muscovite mica is used instead of phlogopite mica.

Commercially available grades of mica have a range of particle size distributions. It has been found that the particle size of the mica also has an impact on the dimensional stability and mechanical properties of the ceramic product formed when a composition of the present invention is exposed to elevated temperature. Typically, the mica is selected so that it has a mean particle size of from $15\text{ }\mu\text{m}$ to $250\text{ }\mu\text{m}$. Micas at the lower end of this range (e.g. less than $50\text{ }\mu\text{m}$ mean particle size) result in ceramics that are mechanically stronger but display greater shrinkage that can result in cracking. Thus, micas at the middle and upper end of the range are preferable for use in cable applications or other applications where shape retention is particularly important. If the mean particle size of the mica is too large or the amount of mica present is too high, the resultant composition tends to be difficult to process and form into the desired configuration, for instance by extrusion. In addition, the mechanical properties of crosslinked silicone polymers containing coarser particle size grades of mica or high mica levels are poorer.

The mica may be surface treated with a silane coupling agent in order to enhance the compatibility of the mica with the silicone polymer.

In accordance with the present invention the selection of the appropriate mica type, mean particle size and mica level will depend on the intended application, the required processing properties of the composition, the required mechanical properties of the crosslinked composition, and the required strength and dimensional stability of the
5 resulting ceramic.

The preferred levels of mica are 30% by weight or less. For fire resistant cable and non-cable applications where dimensional stability is important, the mean particle size of the mica is preferably in the range of 50-200 μm . Muscovite mica is the type generally
10 preferred for those applications, but greater mechanical strength after firing at 1000°C can be obtained using phlogopite mica.

In one embodiment the compositions of the present invention consist essentially of the silicone polymer, mica and crosslinking agent. This means that the compositions do not
15 contain any other component which would materially effect the properties of the composition and/or the ceramic formed upon heating the composition to elevated temperatures.

Surprisingly, it has also been found that the presence of low levels of glass additive in the
20 compositions of the present invention markedly improves the mechanical strength of the ceramic formed on heating the composition. Accordingly, in another embodiment, the present invention provides a composition comprising:

a silicone polymer;
mica in an amount of up to 30% by weight based on the total weight of the composition;
25 and
a glass additive in an amount of up to 8% by weight based on the total weight of the composition.

The glass additive is particularly effective at extending the range of temperatures that
30 result in formation of ceramics with good mechanical properties, thereby improving the performance of these compositions in passive fire protection applications. The type and

mean particle size of the mica is typically selected based on the intended use of the composition, as already described.

The glass additive may take a variety of forms such as powder, frits or fibres. Mixtures of one or more of these may be used. Preferably, the composition comprises glass frits. Irrespective of form, the glass additive preferably has a softening point below 1050°C, for example below 800°C, and most preferably between 300 and 800°C. The softening point of a glass is defined by the temperature at which the viscosity of the glass equals $10^{7.6}$ poise.

The glass additive may be one or a combination of silicate, borate, phosphate and/or lead based glass systems. Suitable glass additives are commercially available.

Without wishing to be bound by theory, it is believed that the presence of the glass additive results in a stronger ceramic material being formed if the composition of the invention is exposed to elevated temperature due to the glass softening or melting at a lower temperature than the other components. This is thought to assist in "binding" the decomposition products of the silicone polymer and/or the mica particles together. In this way formation of a coherent ceramic product is improved and it is possible to reduce the temperature required to form a comparatively strong ceramic material. If the levels of glass additive are 8% or less, the additive does not adversely affect dimensional stability. Compositions in accordance with the present invention may yield a coherent ceramic product that has essentially the same shape and volume as the composition before being exposed to elevated temperature. Such compositions can be described as retaining near net shape.

The softening point of the glass has an impact on the properties of the ceramic formed at elevated temperatures. Glasses with relatively low softening points provide enhanced mechanical strength at lower temperatures than glasses with relatively high softening points. The mechanical strength after cooling from high temperatures (e.g. 1000°C) may be greater if a high softening point glass additive is used. A blend of glass additives

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having low and high softening points may be used to provide a composition which yields a ceramic on heating which develops good mechanical properties after exposure to a large range of temperatures.

- 5 The proportion of mica and glass additive in the compositions of the present invention are within the stated ranges. For cable applications, where the electrical resistivity of the composition is important, the levels of mica and/or glass additive must be selected carefully. For a given composition, if the level of mica is too high electrical integrity problems arise due to an unacceptable reduction in electrical resistivity of the composition and/or from dielectric breakdown when the compositions are subjected to high
10 temperatures for an extended period of time. At high temperatures alkali metal ions from either the mica or the glass additive in the liquid phase tend to provide conductive pathways, resulting in the need to limit the level of mica and/or the level of glass additive. For this reason it may also be appropriate to select a glass additive having a low alkali
15 metal content. Unexpectedly, it has also been found that the glass additive may improve the adhesion between an adjacent metal surface (eg the cable conductor) and the ceramic formed upon heating of compositions of the present invention.

- 20 In one embodiment the compositions of the present invention consist essentially of the silicone polymer, mica, glass additive and crosslinking agent. This means that the compositions do not contain any other component which would materially effect the properties of the composition and/or the ceramic formed upon heating the composition to elevated temperature.

- 25 In one embodiment of the present invention it has been found that incorporation of a relatively high concentration of glass additive in the composition of the invention can lead to formation of a glassy surface layer when the composition is ceramified (at elevated temperature) and cooled. Desirably, this surface layer has been found to confer improved water resistance to the ceramic formed. The formation of such a surface layer, and
30 associated enhanced water resistance, is particularly beneficial in electrical cable applications because ingress of water (used to quench a fire) through the ceramic is likely

to lead to electrical shorting. Of course, the potentially detrimental effects of high levels of glass additive (shrinkage and electrical conductivity) must be taken into account. The amount of glass additive required to form the glassy surface layer when the composition forms a ceramic may vary depending upon the other ingredients present in the composition. However, in general terms the glass additive is present in a weight ratio of mica: glass additive of from 10:1 to 2:1. Typically, this amounts to a proportion of glass additive of from 2 to 8% by weight based on the total weight of the composition. The total amount of glass additive may be derived from a single source or from more than one source. For instance, the totality of glass additive may be made up of glass frits, fibres and/or particles of the same or different type of glass. A similar effect may be observed by using a relatively high concentration of mica, for example about 25% by weight, since this too can lead to an increase in the liquid phase formed during heating.

The mechanism by which the glassy surface layer (skin) is formed is not clearly understood, although glass flow is clearly required in order to form the (densified) glassy surface layer. This means that the melting temperature of the glass additive (and/or mica as the case may be) must be selected so that some flow is possible at the ceramic-forming temperature. It may be desirable to incorporate a variety of glass additives having different melting points to achieve skin formation and the desirable mechanical properties achieved by melting of glass additives. The mechanism for formation of the glassy surface layer may be associated with surface tension effects between the molten glass and its local environment. One possible explanation for migration and aggregation of glass to the surface of the formed ceramic is that the surface energy at the glass/atmosphere interface is lower than that of the energy at the interface between the molten glass and the bulk of the composition. This being so, the molten glass migrates to the lower energy interface.

Surprisingly, it has also been found that incorporation of certain additional components can promote formation of the glassy surface layer in the ceramic. Accordingly, the composition of the invention may further comprise one or more metal oxides selected from zinc oxide, calcium oxide and magnesium oxide, or compounds which yield such oxides when exposed to temperatures at which ceramic formation typically takes place. Again,

the underlying theory as to why the metal oxide enhances formation of the glassy surface layer is not fully understood, although it may be due to the fact that the metal oxide lowers further the surface tension of the glass and/or the surface energy of the glass/atmosphere interface, thereby promoting migration and aggregation of the molten glass. Typically, the metal oxide or oxide precursor is present in the composition in an amount of from 1 to 10% by weight, preferably from 1 to 5% by weight (as metal oxide).

It has been found that the thickness of the composition may have an impact on the formation of the water resistant surface layer. This is believed to be due to volume effects, with more glass (and/or mica) being available for formation of a suitably thick surface layer when the thickness of the composition is greater. It has been observed in fact that a thicker sample of a composition yields a more water resistant surface layer than a thinner sample of the same composition.

Water resistance can also be improved by the addition of inorganic fibres which do not melt at 1000°C. Alumino-silicate fibres are preferred and can be used at levels of up to 5% by weight.

Other components may be incorporated into the compositions of the present invention. These other components include fire retardant materials, inorganic fibres or other fibre reinforcing materials, materials that reduce thermal conductivity (eg exfoliated vermiculite), chemical foaming agents (which serve to reduce density, improve thermal characteristics and further enhance noise attenuation), extending non-reactive fillers, silica, and intumescent materials (to obtain a composition that expands upon exposure to fire or elevated temperature). Suitable intumescent materials include natural graphite, unexpanded vermiculite or unexpanded perlite. Other types of intumescent precursors may also be used.

The compositions of the present invention may be prepared by blending and heating the various components. Heating is required for peroxide crosslinking of the silicone polymer to form a silicone elastomer. Any conventional compounding equipment may be used. If

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the composition has relatively low viscosity, it may be processed using dispersing equipment, for instance of the type used in the paint industry. Materials useful for cable insulation applications are of higher viscosity (higher molecular weight) and may be processed using a two roll mill, internal mixers, twin-screw extruders and the like.

- 5 Depending upon the type of crosslinking agent/catalyst added, the composition can be cured by exposure to air at 200°C, in an autoclave with high pressure steam, using continuous vulcanisation equipment including a liquid salt bath and, conceivably, by exposure to any medium that will cause the peroxide to decompose, including microwaves, ultrasonics etc.

10

The compositions of the present invention may be used in a large number of applications where fire resistance is desired. For example, the compositions may be used to form a fire resistant building panel or in the manufacture of ceramic products. The composition may be used by itself or together with one or more layers of other materials.

15

The compositions of the present invention may be provided in a variety of different forms, including:

1. As a sheet, profile or complex shape. The composition may be fabricated into
20 these products using standard polymer processing operations, eg extrusion, moulding (including hot pressing and injection moulding). The products formed can be used in passive fire protection systems. The composition can be used in its own right, or as a laminate or composite with another material (for example, plywood, vermiculite board or other). In one application the composition may be
25 extruded into shapes to make seals for fire doors. In the event of a fire, the composition is converted into a ceramic thus forming an effective mechanical seal against the spread of fire and smoke.
2. As a pre-expanded sheet or profile. This form has additional benefits compared
30 with the above, including reduced weight and the capacity for greater noise attenuation and insulation during normal operating conditions. Porosity can be

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incorporated into the material during manufacture of the sheet or profile by thermal degradation of a chemical blowing agent to produce a gas product, or by physically injecting gas into the composition before curing.

3. As an intumescent product, which expands by foaming when exposed to heat or fire. In this application the product can be used, for example, around pipework or penetrations between walls. In the event of a fire the product expands to fill the void and provide an effective plug to prevent the spread of fire. The intumescent material may be in the form of an extrudable paste or a flexible seal.

4. As a mastic material which can be applied (for example from a tube as per a conventional silicone sealant) as a seal for windows and other articles.

5. As a paint, or an aerosol based material, that could be sprayed or applied by with a brush.

The compositions of the present invention may also be used in the manufacture of ceramics. In this aspect, the present invention provides a method for manufacturing a ceramic article comprising a composition as herein described. The method involves shaping said composition to a desired shape and heating to elevated temperatures to thereby degrade the silicone polymer and form a solid material such that a coherent mass is formed after cooling. Other conventional ceramic processing steps, such as sintering, may also be included in this method. The present invention also provides a method for producing ceramics using polymer precursors involving silicone and other organosilicon polymers. In this aspect of the present invention, it has been found that the heating step causes little or no volume reduction in the article. Thus, the firing step can result in the production of near net shapes.

Specific examples of passive fire protection applications where this invention may be applied include but are not limited to firewall linings for ferries, trains and other vehicles, fire partitions, screens, ceilings and linings, structural fire protection [to insulate the

structural metal frame of a building to allow it to maintain its required load bearing strength (or limit the core temperature) for a fixed period of time], fire door inserts, window and door seals, intumescent seals, and compounds for use in high voltage electrical boxes or similar applications.

5

The compositions of the present invention are especially useful in the coating of conductors. The compositions are therefore suitable for the manufacture of electrical cables that can provide circuit integrity in the case of fire. In the design of such cables the compositions can be used as an extruded insulation directly over conductors, as an
10 interstice filler in multi-core cables, as individual extruded fillers added to an assembly to round off the assembly, as an inner layer prior to the application of wire or tape armour or as an outer sheathing layer.

In practice the composition will be extruded onto the surface of a conductor. This
15 extrusion may be carried out in a conventional manner using conventional equipment. Typically the composition will be crosslinked immediately after extrusion. The thickness of the layer of insulation will depend upon the requirements of the particular standard for the size of conductor and operating voltage. Typically the insulation will have a thickness from 0.6 to 3 mm. For example, for a 35mm² conductor rated at 0.6/1kV to Australian
20 Standards would require an insulation thickness of approximately 1.2 mm.

The following examples illustrate the present invention.

The compositions in all examples were based on a commercially available silicone
25 elastomer. The mean particle size of the mica was determined by sieve analysis and, unless otherwise indicated, the mica used was muscovite with a mean particle size of 160 μ m. Glass frit A has a softening point of 430°C and had the analysed composition: SiO₂, 33.5%; Na₂O, 18.2%; K₂O, 10.8%; TiO₂, 19.3%; P₂O₅, 1.8%; V₂O₅, 8.7%. Glass frit B has a softening point of 600°C and had the analysed composition: SiO₂, 39.2%; ZnO, 36.2%;
30 Na₂O, 2.9%; K₂O, 2.2%; CaO, 5.3%; MgO, 0.2%; ZrO₂, 0.8%. Dicumyl peroxide was included in the compositions for effecting thermal crosslinking. All compositions listed in

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the examples are given in %wt/wt. The compositions were made by the procedure described below.

5 A two-roll mill was used to prepare the compositions. The silicone elastomer was banded on the mill (10-20°C) and first mica, and then the glass frits, were added and allowed to disperse by separating and recombining the band of material just before it passed through the nip of the two rolls. When these were uniformly dispersed in the elastomer, the peroxide was added and dispersed in a similar manner.

10 The compositions for the tests in Examples 1-4 were then removed from the mill as a sheet, and then pressed and vulcanized between two 10 mm steel backing plates covered with sheets of 250 micron polyester film in a picture-frame (1.7 mm or 3 mm thick) mould for 30 minutes at 170°C and 7 MPa.

15 Example 1

(A)

Specimens of dimensions 50 mm x 14 mm x 3 mm, made from thermally crosslinked
20 (170°C, 30 minutes, 7 MPa) compositions containing silicone elastomer and peroxide with mica of differing particle sizes were heated to 600°C, 800°C and 1000°C for 30 minutes in air. Mica A is coarse muscovite (mean particle size = 160 µm), mica B is intermediate muscovite (mean particle size = 71 µm), mica B' is intermediate phlogopite (mean particle size = 70 µm) and mica C is fine muscovite (mean particle size = 32 µm). The flexural
25 strength of the cooled samples was determined in three point bend mode using an Instron Universal Testing Machine. The results for muscovite grades A-C (Table 1) show that decreasing the mica particle size increases the measured flexural strength of samples cooled from 600°C, 800°C and 1000°C. The measured increase in flexural strength of the fine mica composition over the coarse mica composition is 69% at 600°C, 50% at 800°C
30 and 124% at 1000°C. Comparison of the results for muscovite and phlogopite of

essentially the same mean particle size (micas B and B') show that at 1000°C the phlogopite containing composition has a much higher flexural strength.

Compositions (%wt/wt)	Flexural Strength (MPa)		
	600°C	800°C	1000°C
Silicone/mica A/peroxide (78:20:2)	0.3	0.7	2.2
Silicone/mica B/peroxide (78:20:2)	0.3	0.8	2.9
Silicone/mica B'/peroxide (78:20:2)	-	0.6	9.3
Silicone/mica C/peroxide (78:20:2)	0.5	1.0	4.9

Table 1 Flexural strength of silicone compositions containing mica grades of differing

5 mean particle size.

- = sample not tested.

(B)

- 10 Experimental cable sections were fabricated with 35mm² compacted copper conductor insulated with silicone/mica/peroxide (68:30:2) compositions made using a coarse (mean particle size = 160 µm) grade of muscovite mica (A) and a finer (mean particle size = 39 µm) grade muscovite (mica D). The insulation on the cables was crosslinked under pressure (170°C, 30 minutes). The cables were then heated at 10°C per minute to 1000°C
- 15 for 30 minutes. Inspection of the fired cables revealed substantial longitudinal and transverse cracking in the ceramic formed from the insulation and exposed conductor on the cable made with the finer mica, a result of excessive shrinkage during formation of the ceramic. The ceramic coating on the cable made with the coarse mica was crack free and no conductor was exposed.

20

(C)

- Flat sheet specimens of dimensions 50 mm x 14 mm x 3 mm, made from thermally crosslinked (170°C, 30 minutes, 7 MPa) compositions containing silicone elastomer and
- 25 peroxide with two different classes of mica of differing particle sizes were heated to

1000°C for 30 minutes. The silicone/mica/peroxide ratio of the compositions was 78:20:2. The results (Table 2) show that for comparable particle sizes, specimens made from phlogopite mica exhibit significantly higher linear shrinkage than the equivalent muscovite mica specimens. This indicates that the use of muscovite mica is preferable to the use of
5 phlogopite mica for the dimensional stability of fired compositions.

Mica Grade	Coarse		Fine	
Mica Class	Muscovite (mica B)	Phlogopite (mica B')	Muscovite (mica C)	Phlogopite
Mean Particle Size	71 µm	70 µm	32 µm	20µm
Linear Shrinkage (%)	2.1	12.8	2.9	13.3

Table 2 The effect of mica class on linear shrinkage of silicone/mica/peroxide specimens fired to 1000°C for 30 minutes.

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The mechanical properties of the crosslinked (170°C, 30 minutes, 7 MPa) compositions shown in Table 3 were determined. The results show that the tensile strength and percent elongation values decrease with increasing mean particle size of the mica in the
15 crosslinked compositions.

Composition	Mean mica particle size (µm)	Tensile Strength (MPa)	Elongation %
Silicone/peroxide (98:2)	na	7.5	295
Silicone/mica D/peroxide (78:20:2)	39	5.8	205
Silicone/mica B/peroxide (78:20:2)	71	4.5	170
Silicone/mica A/peroxide (78:20:2)	160	3.2	25

Table 3 Tensile strength and percent elongation values for crosslinked compositions with differing mean particle size of the mica.

na = not applicable

Example 2

Specimens of dimensions 38.1 mm x 13.3 mm x 1.7 mm, made from thermally crosslinked (170°C, 30 minutes, 7MPa) compositions containing the silicone elastomer and peroxide with 20%wt/wt and 30%wt/wt mica and differing levels of a low softening point glass frit, were heated to the temperatures indicated at 10°C per minute and then held at either 600°C or 1030°C for 30 minutes in air. The percentage changes in volume for the cooled samples are given in Table 4 below. The results show that if the levels of the glass frits are increased to 10%, there is significant shrinkage of the compositions at 1030°C.

Composition (%wt/wt)	600°C	1030°C
Silicone/mica/peroxide (78:20:2)	+7	+1
Silicone/mica/glass frit A/peroxide (73:20:5:2)	+7	0
Silicone/mica/glass frit A/peroxide (70.5:20:7.5:2)	-1	-7
Silicone/mica/glass frit A/peroxide (68:20:10:2)	+6	-22
Silicone/mica/glass frit A/peroxide (63:30:5:2)	+7	-1
Silicone/mica/glass frit A/peroxide (58:30:10:2)	+2	-45

Table 4 The effect of mica levels, glass frit levels and firing temperature on percentage volume change.

Example 3

Specimens of dimensions 38.1 mm x 13.3 mm x 1.7 mm, made from thermally crosslinked (170°C, 30 minutes, 7MPa) compositions containing silicone elastomer and peroxide with 20%wt/wt and 30%wt/wt mica and differing levels of a low softening point glass frit (A) were heated to 600°C for 30 minutes in air. The penetration load of the cooled samples was determined using an Instron Universal Testing Machine with a 90° cone tip indenter attached to the upper loading frame. The penetration load is the peak load attained as the indenter penetrates and subsequently fractures the specimen. The flat fired ceramic specimen was placed on a wooden flat plate, to minimise the damage to the cone tip caused by the bottom steel component, and the penetration load was measured using a speed of 1

mm/min. The results (Table 5) show that there is a synergistic improvement in the penetration load by using a combination of the mica and the low softening point glass frit. Thus 20% mica alone and 7.5% glass frit alone give penetration loads of 26 and 4 N respectively, but the combination of the two gives a value of 45 N. The penetration load of the compositions containing both mica and glass frit increases as the level of glass frit increases.

Composition (%wt/wt)	Penetration load (N)
Silicone/glass frit A/peroxide (90.5:7.5:2)	4
Silicone/mica/peroxide (78:20:2)	26
Silicone/mica/glass frit A/peroxide (73:20:5:2)	40
Silicone/mica/glass frit A/peroxide (70.5:20:7.5:2)	45
Silicone/mica/ glass frit A/peroxide (68:20:10:2)	56

Table 5 The effect of mica levels and low softening point glass frit levels on penetration load for specimens cooled after heating to 600°C for 30 minutes.

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Example 4

Specimens of dimensions 50 mm x 14 mm x 3 mm, made from thermally crosslinked (170°C, 30 minutes, 7 MPa) compositions containing silicone elastomer and peroxide with mica and differing levels of either low or high softening glass frits (frit A and B respectively) were heated to 600°C, 800°C and 1000°C for 30 minutes in air. The flexural strength of the cooled samples was determined in three point bend mode using an Instron Universal Testing Machine. The results (Table 6) show that the combination of silicone/mica/glass frit produces synergistic improvements in flexural strength over silicone/mica and silicone/glass frit compositions. Compositions of 2.5% glass frit A in silicone and 20% mica in silicone fired to 1000°C produce flexural strengths of 0.5 and 2.2 MPa respectively. The combination of silicone/mica/glass frit produces flexural strengths of 3.2 MPa using 2.5% of frit A and 5.8 MPa using 2.5% of frit B. The results show that the high softening point glass is more effective in enhancing flexural strength after firing at

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this high temperature, and that reducing the content of frit B to 1.25% reduces the flexural strength to 4.2 MPa.

For samples fired to 800°C, the results show that the addition of a high softening point glass frit (frit B) provides no strength improvement over a silicone/mica composition. However, the addition of a low softening point glass frit (frit A) to silicone/mica results in a three-fold increase in the flexural strength of samples fired to 800°C (0.7 MPa vs. 2.1 MPa).

Compositions (%wt/wt)	Flexural Strength (MPa)		
	600°C	800°C	1000°C
Silicone/peroxide (98:2)	*	*	0.1
Silicone/glass frit A/peroxide (95.5:2.5:2)	*	0.5	0.5
Silicone/mica/peroxide (78:20:2)	0.3	0.7	2.2
Silicone/mica/glass frit A/peroxide (75.5:20:2.5:2)	-	2.1	3.2
Silicone/mica/glass frit B/peroxide (76.25:20:1.25:2)	0.3	0.7	4.2
Silicone/mica/glass frit B/peroxide (75.5:20:2.5:2)	0.4	0.6	5.9

Table 6 The effect of mica and glass frit additions on the flexural strength of specimens cooled after heating to 600°C, 800°C and 1000°C for 30 minutes in air.

* = samples too weak to be tested;

- = sample not tested

Example 5

Samples of the thermally crosslinked (170°C, 30 minutes) compositions listed in Table 4 were heated at 10°C per minute to 1000°C. During heating a voltage was placed across the samples and the current flow in the circuit was monitored by an ammeter. The results were then converted to volume resistivities by applying Ohm's Law. It is known that electrical resistivity decreases with increasing temperature, especially in glasses which contain mobile ions. A decrease in volume resistivity (increase in current flow) with increasing

temperature is observed over the measured temperatures of 900°C, 950°C and 1000°C for all of the different compositions as shown in Table 7 below.

The addition of alkali-containing mica to silicone causes a reduction in volume resistivity.

- 5 The reduction in volume resistivity is slightly greater if phlogopite mica (e.g. mica B') is used instead of muscovite mica. The addition of a high-alkali, low softening point glass frit (frit A) to silicone/mica causes a large reduction in volume resistivity, a result of the high levels of sodium and potassium in the frit. When the high-alkali frit is replaced by a high softening point, low-alkali frit (frit B), the reduction in volume resistivity for
- 10 silicone/mica is only modest. Reducing the level of mica in a silicone/mica/glass frit composition by partial replacement of the mica with an alkali-free silicate filler has the effect of increasing the resistivity of the compound.

Composition (%wt/wt)	Volume Resistivity (ohm-cm)		
	900°C	950°C	1000°C
Silicone/peroxide (98:2)	High, off scale	2.0×10^7	1.0×10^7
Silicone/mica/peroxide (68:30:2)	3.1×10^7	4.5×10^6	1.8×10^6
Silicone/mica B'/peroxide (68:30:2)	5.6×10^6	2.1×10^6	5.6×10^5
Silicone/mica/glass frit A/peroxide (65.5:30:2.5:2)	1.0×10^5	6.0×10^4	3.2×10^4
Silicone/mica/glass frit B/peroxide (65.5:30:2.5:2)	6.3×10^6	2.3×10^6	6.7×10^5
Silicone/mica/alkali-free filler/glass frit B/peroxide (65.5:20:10:2.5:2)	1.5×10^7	5.21×10^6	1.4×10^6

Table 7 Effect of level of mica and glass frits on the electrical volume resistivity at high

15 temperatures.

Example 6

Performance in a fire test.

- 5 Experimental cables were made with 1.5mm^2 plain copper conductors insulated in one case with a silicone/mica/peroxide (78:20:2) composition and in another with a silicone/mica/glass frit B/peroxide (76.75:20:1.25:2) composition. The compositions were crosslinked during production. These insulated conductors were twisted together and sheathed with a commercially available, halogen-free fire retardant thermoplastic
- 10 sheathing material. The cables were tested while energised at 240 Volts (phase to earth) in the fire and mechanical shock test as described in the British Standard test BS6387 at 950°C for 15 minutes with a severe mechanical shock every 30 seconds. It was found that the conductors insulated with the silicone elastomer and mica composition failed this test, while the conductors insulated with the silicone elastomer, mica and glass frit composition
- 15 successfully withstood the conditions.

Example 7

The following compositions were prepared:

- 20
- Composition 1 – Silicone/mica/peroxide (78:20:2)
 - Composition 2 – Silicone/mica/glass frit A/peroxide (70.5:20:7.5:2)

These were compression moulded with heating (150°C , 30 minutes) into panels (1200 mm x 900 mm x 10 mm) that were tested to assess relative fire resistance as measured by integrity failure according to the Australian Standard AS 1530 Part 4: Fire resistance tests

25 of elements of building construction – Pilot furnace test. The panels were held up against the door frame of a gas-fired furnace that operates under positive pressure, and the samples were tested to the standard cellulose heating curve specified in the test which targets temperatures rising to 1150°C over 240 minutes. Integrity failure is relevant for comparing materials that are intended to resist the passage of flame and was measured as the point

30 where flame burst through first occurred; for composition 1 this was 24 minutes (when the average measured furnace temperature was 821°C) and for composition 2 this was 97

- 24 -

minutes (when the average measured furnace temperature was 1023°C). The results show that addition of the glass frit markedly improves performance as a fire barrier material.

Example 8

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A sample of compound 2 from Example 7 was extruded into a door seal, crosslinked (170°C, 30 minutes) and fired at 1000°C. The sample demonstrated a high degree of structural integrity, maintaining the shape of the door seal after firing and displaying only minor shrinkage.

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